栗柄金粉蕨的黄酮类成分 *

许云龙，郑　兴，何以能

（中国科学院昆明植物研究所植物化学开放研究室，云南 昆明　650204）

摘要： 从栗柄金粉蕨（*Onychium lucidum*）地上部分的甲醇抽提物中分到 10 个成分，经详细的一维、二维核磁数据分析，它们被鉴定为：木犀草甙（**1**），3，7 - 二甲基槲皮素（**2**），高山甙 B（**3**），金粉蕨素（**4**），栗柄醇（**5**），金粉蕨醇 B（**6**），β - 谷甾醇（**7**），胡萝卜甙（**8**），齐墩果酸（**9**）和蔗糖（**10**）。栗柄醇系新成分。1，2，9 系首次由金粉蕨属分到。
关键词： 中国蕨科；栗柄金粉蕨；黄酮；黄酮甙；甲氧基环多醇。

中图分类号： Q 946　　　**文献标识码：** A　　　**文章编号：** 0253 - 2700(1999)04 - 0497 - 08

Flavonoids of *Onychium lucidum*

XU Yun - Long, ZHENG Xing, HE Yi - Neng

（ *Laboratory of Phytochemistry，Kunming Institute of Botany，The Chinese Academy of Sciences，Kunming 650204* ）

Abstract： Ten compounds were isolated from the methanolic extract of the aerial parts of *Onychium lucidum* These compounds were identified as luteoloside (**1**), 3, 7 - dimethylquercetin (**2**), contigoside B (**3**), onychin (**4**), lucidol (1β - methoxy - 2β, 3α, 4β, 5α, 6β - pentahydroxycyclohexane) (**5**), onychiol B (**6**), β - sitosterol (**7**), daucosterol (**8**), oleanolic acid (**9**) and sucrose (**10**). Compound **5** is a new constituent, while **1**, **2** and **9** were isolated from the genus *Onychium* for the first time. Their structures were elucidated on the basis of detailed spectroscopic analysis, in particular, two - dimensional NMR (^{1}H - ^{1}H COSY; ^{1}H - ^{1}H NOE; ^{1}H - ^{13}C COSY, COLOC) data.

Key words： Sinopteridaceae; *Onychium lucidum* ; Flavone and flavone glycoside; Methoxycyclopolyols.

Onychium is a small genus with about 10 species belonging to the family Sinopteridaceae. *Onychium* , mainly distributed in eastern Asia, is used in traditional Chinese medicine for enteritis, jaundice, flu and fever and as toxicide (Zhou, 1988). The compounds so far isolated from *Onychium* include flavonoids, indanoids, chalcone and diterpenoids (Xu *et al* , 1993; Akabori *et al* , 1980; Sengupta *et al* , 1976; Hasegawa *et al* , 1974; Banerji *et al* , 1974, Ramakrishanan *et al* , 1974)

The phytochemical study on *Onychium lucidum* has not been reported. The present paper describes the isolation, structural elucidation and identification of these ten constituents from *Onychiun lucidum*.

Results and Discussion

Luteoloside (1) $C_{21}H_{20}O_{11}$ [M]$^+$ 448, has strong IR absorption bands for hydroxyl groups (3420 – 3100 cm^{-1}) and the characteristic peaks due to the flavonol skeleton (1646, 1585 cm^{-1}). This was further supported by typical UV absorption at 256, 266, 348 nm (Nomura *et al* , 1978). The ^{13}C NMR data (Table 2) also revealed the presence of a flavone and a glucose unit. Its aglycone was very similar to those of 3′, 4′, 5, 7 – tetrahydroxyflavone (luteolin) in the ^{13}C NMR spectra (Wagner *et al* , 1976). Comparison of the ^{1}H NMR spectra of **1** with that of luteolin showed the presence of δ 6.78 for 3 – H signal and the extreme downfield characteristic δ 12.98 for 5 – OH signal due to the intramolecular hydrogen bonding (Roitman *et al* , 1993). In addition, if glucose unit was attached to C – 3′or C – 4′, then the signals of C – 2′and C – 4′ or C – 3′ and C – 5′ would be downfield shifted (Markham *et al* , 1978). Therefore, glucose unit only could be attached to the 7 – hydroxyl group. On the basis of the above evidence, we assigned 1 as luteolin – 7 – glucoside (Kokkalou *et al* , 1988), namely 2 -(3, 4 – dihydroxyphenyl) – 7 -(– D – glucopyranosyloxy) – 5 – hydroxy – 4H – 1 – Benzopyran – 4 – one.

3, 7 – Dimethylquercetin (2), $C_{17}H_{14}O_7$ [M]$^+$ 330 have strong IR absorption bands for hydroxyl groups (3390, 3140 cm^{-1}) and the characteristic peaks due to the flavonol skeleton (1640, 1575 cm^{-1}). This was further supported by typical UV absorption at 256, 296, 356 nm (Nomura *et al* , 1978). The ^{13}C NMR data (Table 2) also revealed the signals of a carbon skeleton of a flavone and two methoxyl groups. The flavonol has very similar ^{13}C NMR data to those of 3, 3′, 4′, 5, 7 – pentahydroxyflavone (quercetin) (Wagner *et al* , 1976). The locations attached of two methoxyl groups were deduced as follows. Comparison of the ^{1}H NMR spectra of 2 with that of quercetin was showed that the two hydroxyl groups at the C – 3 and C – 7 in quercetin had replaced, the two methoxyl groups at C – 3 and C – 7 in 2, according to the lack 7 – OH (ca. δ 9.5) and 3 – OH (ca. δ 10.6) signals and the presence of 12.68 for 5 – OH signal due to the intramolecular hydrogen bonding in 2 (Roitman *et al* , 1993). In addition, the downfield shift of the C – 2 and C – 4 signals from δ 146.9 and 175.9 in quercetin to δ 155.91 and 177.95 in 2 and the upfield shift of the C – 6 and C – 8 signals from δ 98.3 and 93. 5 in quercetin to δ 97.62 and 92.13 in 2 also were confirmed that the two methoxyl groups were attached the C – 3 and C – 7 position in 2, respectively. Therefore, the structure of 2 was assigned as 3, 7 – dimethylquercetin, namely 2 -(3, 4 – dihydroxyphenyl) – 3, 7 – dimethoxyl – 5 – hydroxy – 4H – 1 – Benzopyran – 4 – one.

Contigoside B (3), $C_{21}H_{20}O_{12}$, [M]$^+$ 464. The ^{13}C NMR data revealed the presence of a flavone and a glucose unit. Its aglycone unit was very similar to those of 3,3′,4′,5,7 – pentahydroxyflavone (quercetin) in ^{13}C NMR data (Wagner *et al* , 1976). Comparison of the ^{1}H NMR sprctra of 3 with that of quercetin showed the lack of the extreme downfield characteristic signal for 3 – OH (～ 10.6) due to the intramolecular hydrogen bonding (Roitman *et al* , 1993). Therefore, this glucose unit could be suggested to the 3 – hydroxyl group. This conclusion was supported by ^{13}C NMR data which showed the two the downfield shift of the C – 2 and C – 4 signals from δ 146.9 and 175.9

in quercetin to δ 156.13 and 177.37 in **3** (Markham *et al*, 1978). On the basis of the above evidence, **3** was determined as quercetin – 3 – glucoside (Xu *et al*, 1999).

Onychin (**4**), $C_{27}H_{32}O_{13}$, M 564. The ^{13}C NMR data revealed the presence of a flavanone and a disaccharide moiety. Its aglycone unit has almost the same ^{13}C NMR data to those of 5, 7 – dihydroxyflavanone (pinocembrin) (Wagner *et al*, 1976). The disaccharide unit also has almost the same ^{13}C NMR data to those of a β – D – glucopyranose$^{2\rightarrow1}\alpha$ – L – rhamnoside unit (Markham *et al*, 1978). In addition, the extreme downfield δ 12.46 signal could be assigned to 5 – OH due to the intramolecular hydrogen bonding. Therefore, disaccharide unit is attached to the 7 – hydroxyl groups. This conclusion was supported by ^{13}C NMR data which showed the downfield shift of the C – 6, C – 8 and C – 10 signals from δ 96.1, 95.1 and 101.9 in pinocembrin to δ 97.85, 96.23 and 104.35 in **4** (Wagner *et al*, 1976). In addition, this conclusion was further confirmed by the detailed ^1H – ^1H COSY, ^1H – ^{13}C COSY and COLOC analyse. So, we assigned **4** as onychin (Xu *et al*, 1993).

Lucidol (**5**), $C_7H_{14}O_6$, $[M]^+$ 194, was found to have five secondary hydroxyl groups and a secondary methoxy group on the following spectroscopic data: IR ν_{max}^{KBr} cm^{-1}: 3390 – 3150, ^{13}C NMR: δ 87.44 (1C, d), 74.32 (2C, d), 74.01 (2C, d), 73.88 (1C, d), 60.76 (1C, q, OMe); ^1H NMR: δ 4.76 (1H, t, J = 2.8Hz), 4.67 (2H, t, J = 9.4Hz), 4.09 (2H, dd, J = 9.4, 2.8Hz), 3.96 (3H, s, MeO), 3.58 (1H, t, J = 9.4Hz); The above data suggested that **5** has a cyclohexane nucleus as a basic skeleton. The position of six oxygen functional groups were deduced as follows. The signal at δ 4.76 indicated the existence of methoxy group in axial orientation. The symmetrical signals at δ 4.67 and 4.09 indicated that the four hydroxyl groups are possessed symmetrically in equatorial orientations. The signal at δ 3.58 indicated that the last hydroxyl group also is in equatorial orientation. Thus, the chemical structure of 5 could be represented as 1β – methoxy – 2β, 3α, 4β, 5α, 6β – pentahydroxycyclohexane.

Onychiol B (**6**), $C_{20}H_{32}O_3$ $[M]^+$ 320, showed the presence of three methyl groups, six methylene groups, five methine groups, two quaternary carbons, and four olefinic carbons in the ^{13}C NMR spectrum. So, **6** would have a three – cyclic skeleton. The IR absorption bands were revealed the presence of hydroxyl groups (3280, 3220, 3100 cm^{-1}) and double bonds (1645, 980, 963 cm^{-1}). The extreme upfield 7.87 ppm signal for 5a – Me due to the intramolecular shielding effect of two adjacent hydroxyl is characteristic of onychiol B. The data of MS, ^1H and ^{13}C NMR of **6** were in good agreement with those of onychiol B reported previously (Hseu *et al*, 1980), suggesting that compound **6** was onychiol B.

Experimental

General Kofler melting points were uncorrected; IR were recorded on KBr discs with a Perkin – Elmer 577 spectrometer. UV was obtained in EtOH on a UV – 210A spectrometer. EIMS (positive) were measured on a VG Auto Spec – 3000 spectrometer with direct inlet 70 or 20 eV. NMR were run on a Bruker AM – 400 spectrometer using TMS as internal. standard; chemical shift values

are reported in δ (ppm) units (pyridine – d_5 and $CDCl_3$). Coupling constants (J) were expressed in Hz.

Plant material The aerial parts of *Onychium lucidum* were collected in Shiyang, Dayau County, Yunnan, China in August, 1989, and were identified by Prof. S. K. Wu, a botanist of Our Institute. A voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica.

Extraction and isolation 2 kg dried and powdered of *Onychium lucidum* were extracted with MeOH three times at room temperature for a week, after removal the solvent in vacuum, the residue was subjected on Si gel column chromatography and eluted with gradient $CHCl_3$ – CH_3COCH_3 and $CHCl_3$ – MeOH system. Ten compounds, luteoloside (1) (14 mg, 0.0007%), 3, 7 – dimethoxyquercetin (2) (10 mg, 0.0005%), contigoside B (3) (11 mg, 0.0006%), onychin (4) (2.2 g, 0.11%), and 1β – methoxy – 2β, 3α, 4β, 5α, 6β – pentahydroxycyclohexane (5) (16 mg, 0.0008%), onychiol B (6) (15 mg, 0.0008%), β – sitosterol (7), daucosterol (8), oleanolic acid (9) and sucrose (10), were obtained (See Figure 1). Some components were further purified by recrystallization and prep. TCL (silica gel).

Luteoloside (1), $C_{21}H_{20}O_{11}$ M 448, yellow needle crystals (MeOH), mp. 259 ~ 261℃; $UV\lambda_{max}^{EtOH}$ (logε): 256, 266, 348 nm; IR ν_{max}^{KBr} cm^{-1}: 3420 ~ 3100, 1646, 1585, 1485, 1436, 1365, 1330, 1253, 1167, 1075, 1020, 850, 832, 775, 740, 620; EIMS 70ev m/z (%): 286 (M – Glc, 80), 258 (8), 229 (5), 153 (20), 144 (4), 134 (13), 124 (9), 115 (3), 105 (25), 91 (10), 73 (35), 60 (100); ^{1}H NMR (DMSO – d_6, ppm) δ: See Table 1; ^{13}C NMR (DMSO – d_6,) δ: See Table 2.

3, 7 – Dimethylquercetin (2), $C_{17}H_{14}O_7$ M 330, yellow needle crystals (MeOH), mp. 232 ~ 234℃; $UV\lambda_{max}^{EtOH}$ (logε): 256, 296, 356 nm; IRν_{max}^{KBr} cm^{-1}: 3390, 3140, 1640, 1575, 1480, 1416, 1360, 1332, 1300, 1225, 1200, 1150, 1115, 1010, 908, 815; EIMS 70eV m/z (%): 330 (M$^+$, 100), 312 (20), 301 (11), 287 (39), 271 (4), 257 (5), 244 (6), 203 (8), 167 (17), 151 (15), 137 (27), 122 (13), 109 (B – ring, 15), 95 (17), 81 (12), 69 (20), 55 (27); ^{1}H NMR (DMSO – d_6) δ: See Table 1; ^{13}C NMR (DMSO – d_6,) δ: See Table 2.

Contigoside B (3), $C_{21}H_{20}O_{12}$ M 464, yellow needle crystals (MeOH), mp. 206 ~ 208℃; $UV\lambda_{max}^{EtOH}$ (logε): 258, 366 nm; IRν_{max}^{KBr} cm^{-1}: 3300, 1645, 1595, 1555, 1490, 1432, 1340, 1290, 1260, 1190, 1160, 1105, 1050, 1003, 925, 875, 805; EIMS 70eV m/z (%): 302 (M – 162, 100), 286 (2), 273 (3), 229 (1), 200 (1), 153 (7), 137 (12), 123 (8), 109 (B – ring, 4), 105 (34), 91 (8), 83 (47), 77 (26), 69 (32), 60 (65), 55 (82); ^{1}H NMR (DMSO – d_6) δ: See Table 1; ^{13}C NMR (DMSO – d_6) δ: See Table 2.

Onychin (4), $C_{27}H_{32}O_{13}$ M 564, white needle crystals (MeOH), mp. 279 ~ 280℃; $[\alpha]^{24.5°}$ – 112.93° (MeOH, C 0.29), $UV\lambda_{max}^{EtOH}$ (logε): 213 (4.46), 286 (4.26), 330 (3.50) nm; IRν_{max}^{KBr} cm^{-1}: 3420, 3360, 1655, 1647, 1632, 1574, 1500, 1450, 1394, 1342, 1330, 1322, 1294, 1278, 1226, 1180, 1157, 1085, 1050, 1032, 1015, 994, 978, 885, 844, 820, 775, 750; EIMS

70eV m/z（%）：564（M$^+$, 0.8）, 447（0.4）, 418（M − Rha −, 0.4）, 400（M − Rhamnose, 0.1）, 368（0.8）, 354（0.4）, 256（M − Rha − Glc −, 100）, 238（5）, 179（256 − B − ring, 33）, 153（14）, 152（25）, 129（14）, 104（19）, 85（28）, 77（B − ring, 15）, 71（35）, 55（37）；^{1}H NMR（C$_5$D$_5$N）δ：See Table 1；^{13}C NMR（C$_5$D$_5$N）δ：See Table 2；^{13}C − ^{1}H COSY and COLOC spectra See Table 3.

Lucidol（1β − methoxy − 2β, 3α, 4β, 5α, 6β − pentahydroxycyclohexane）（**5**）, C$_7$H$_{14}$O$_6$ M 194, white amorphous crystals（MeOH）, IRν_{max}^{KBr} cm^{-1}：3390 − 3150, 2900, 2880, 2800, 1430, 1395, 1360, 1320, 1295, 1280, 1255, 1240, 1180, 1120, 1100, 1060, 1045, 1015, 930, 920, 875, 745, 710, 605, 465, 420, 360, 300；FABMS m/z（%）：193（M − 1, 100）, EIMS 70eV m/z（%）：195（M + 1, 24）, 177（M − OH, 7）, 162（M − OH − CH$_3$, 6）, 144（M − OH − CH$_3$ − H$_2$O, 42）, 127（M − 2OH − CH$_3$ − H$_2$O, 13）, 116（47）, 103（40）, 87（94）, 73（100）, 60（74）；^{1}H NMR（C$_5$D$_5$N）δ：4.76（1H, t, J = 2.8Hz, 1α − H）, 4.67（2H, t, J = 9.4Hz, 3β, 5β − H）, 4.09（2H, dd, J = 9.4, 2.8Hz, 2α, 6α − H）, 3.96（3H, s, MeO）, 3.58（1H, t, J = 9.4Hz, 4α − H）；^{13}C NMR（C$_5$D$_5$N）δ：87.44（d, C − 1）, 74.32（d, C − 2）, 74.01（d, C − 3）, 73.88（d, C − 4）, 74.01（d, C − 5）, 74.32（d, C − 6）, 60.76（q, OMe）.
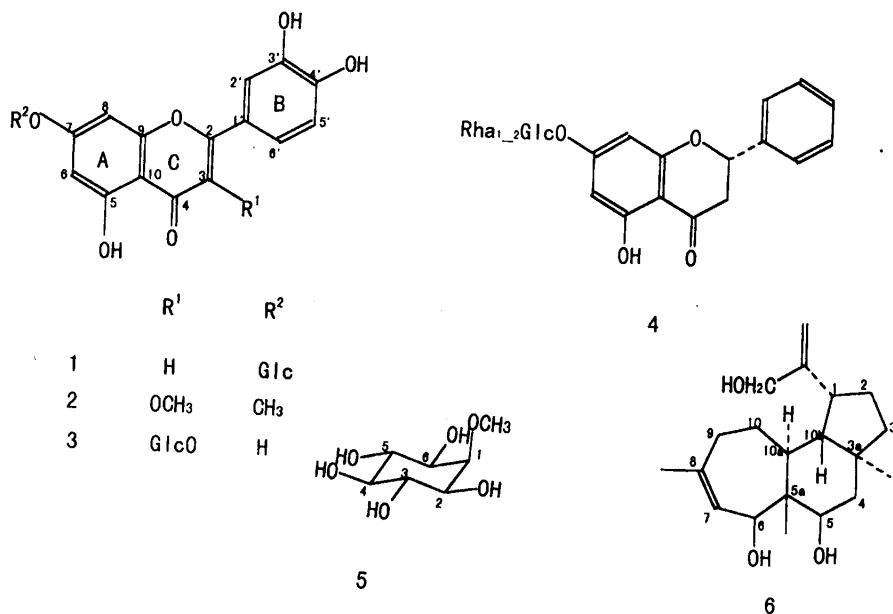
Fig.1　Chemical Constituents of *Onychium lucidum*

Onychiol B（**6**）, C$_{20}$H$_{32}$O$_3$ M 320, white cubic crystals（MeOH）, mp. 209 ~ 210℃；IRν_{max}^{KBr} cm^{-1}：3280, 3220, 3100, 1645, 1468, 1445, 1380, 1354, 1308, 1180, 1154, 1068, 1035, 1026, 1000, 980, 963, 933, 903；EIMS 70eV m/z（%）：320（M$^+$, 3）, 305（0.5）, 287（2）, 269（1）, 201（7）, 185（20）, 175（11）, 159（18）, 145（22）, 133（20）, 119（40）, 105（37）, 91（51）, 84（54）, 79（45）, 67（30）, 55（70）, 41（100）；^{1}H NMR（C$_5$D$_5$N）δ：7.85,

6.64, 5.19 (each 1H, br s, 3 × OH), 5.75 (1H, br s, 7 - H), 5.50, 5.11 (each 1H, br s, C = CH$_2$), 4.86 (1H, br s, 6α - H), 4.48 (1H, dd, 11.6, 3.9, 5α - H), 4.33, 4.28 (each 1H, ABd, 14.6, - CH$_2$ - OH), 2.70 (1H, m, 1β - H), 1.73 (3H, s, 8 - Me), 1.25 (3H, s, 3a - Me), 1.15 (3H, s, 5a - Me); ^{13}C NMR (C$_5$D$_5$N) δ: 51.43 (d, 1 - C), 30.95 (t, 2 - C), 34.48 (t, 3 - C), 41.45 (s, 3a - C), 46.09 (t, 4 - C), 74.81 (d, 5 - C), 45,75 (s, 5a - C), 82.00 (d, 6 - C), 133.07 (d, 7 - C), 136.25 (s, 8 - C), 41.94 (t, 9 - C), 24.33 (t, 10 - C), 40.30 (d, 10a - C), 44.61 (d, 10b - C), 155.40 (s, > C = CH$_2$), 106.71 (t, > C = CH$_2$), 66.32 (t, - CH$_2$OH), 25.66 (q, 8 - Me), 22.44 (q, 3a - Me), 7.87 (q, 5a - Me).

Table 1 ^{1}H NMR spectra data of compound (1), (2), (3) and (4) in DMSO - d$_6$

Hydrogen	1	2	3	4*
H - 3	6.78 br s			
H - 6	6.74 d, 1.6	6.69 d, 2.0	6.39 d, 1.6	6.73 d, 1.6
H - 8	6.43 d, 1.6	6.35 d, 2.0	6.19 d, 1.6	6.67 d, 1.6
H - 2′	7.45 d, 2.4	7.58 d, 2.0	7.58 d, 2.4	7.55 d, 7.6
H - 3′				7.41 t, 7.6
H - 4′				7.36 t, 7.6
H - 5′	6.89 d, 7.8	6.90 d, 8.4	6.83 d, 7.8	7.41 t, 7.6
H - 6′	7.43 dd, 7.8, 2.4	7.47 dd, 8.4, 2.0	7.57 dd, 7.8, 2.4	7.55 d, 7.6
5 - OH	12.98 s	12.68 s	12.63 s	12.46 s
H - 2β				5.40 dd, 12.8, 2.8
H - 3α				3.20 dd, 17.2, 12.8
H - 3β				2.89 dd, 17.2, 2.8
Glc - 1 - H	5.07 d, 7.2		5.45 d, 7.6	5.70 d, 7.6
Glc - H$_6$	3.71 - 3.17 (6H)		3.58 - 3.07 (6H)	
3 - OMe		3.85 s		
7 - OMe		3.78 s		
Rha - 1 - H				6.38 s
Rha - H$_4$				
Rha - Me				1.78 d, 6.0

* In C$_5$D$_5$N

Table 2 ^{13}C NMR spectra data of compound (1), (2), (3) and (4) in DMSO - d$_6$

Carbon	1	2	3	4*
2	164.40 s	155.91 s	156.31 s	79.40 d
3	103.09 d	137.82 s	133.32 s	43.35 t
4	181.76 s	177.95 s	177.38 s	196.52 s
5	161.05 s	160.88 s	161.18 s	164.43 s
6	99.49 d	97.62 d	98.60 d	97.85 d
7	162.88 s	165.04 s	164.12 s	166.22 s
8	94.68 d	92.13 d	93.43 d	96.23 d
9	156.85 s	156.19 s	156.27 s	163.32 s
10	105.28 s	105.10 s	103.90 s	104.35 s
1′	121.32 s	120.57 s	121.13 s	139.24 s
2′	113.49 d	115.49 d	115.15 d	126.75 d
3′	145.69 s	145.18 s	144.73 s	129.07 d

续表 2

Carbon	1	2	3	4 *
4'	149.84 s	148.75 s	148.39 s	128.98 d
5'	115.91 d	115.64 d	116.16 d	129.07 d
6'	119.06 d	120.57 d	121.51 d	126.75 d
Glucose				
1	99.92 d		100.94 d	99.40 d
2	73.06 d		74.05 d	77.80 d
3	77.10 d		77.44 d	79.07 d
4	69.56 d		69.92 d	74.01 d
5	76.34 d		76.48 d	78.75 d
6	60.60 t		60.95 t	62.03 t
Rhamnose				
1				102.36 d
2				72.31 d
3				72.68 d
4				71.10 d
5				69.81 d
CH$_3$				18.78 q
3 – OCH$_3$		59.57 q		
7 – OCH$_3$		55.95 q		

* in C$_5$D$_5$N

Table 3 ^{13}C – ^{1}H COSY and COLOC spectra of onychin (4) in C$_5$D$_5$N

Assignment	^{1}H NMR	^{13}C NMR	COLOC observed
H – 2β	5.40 dd, 12.8, 2.8	79.40 d	C – 4, C – 2
H – 3α	3.20 dd, 17.2, 12.8	43.35 t	C – 4,
H – 3β	2.89 dd, 17.2, 2.8		
H – 6	6.73 d, 1.6	97.85 d	C – 5, C – 7, C – 8, C – 10
H – 8	6.67 d, 1.6	96.23 d	C – 7, C – 9, C – 10
H – 2', 6'	7.55 d, 7.6	126.75 d	
H – 3', 5'	7.41 t, 7.6	129.07 d	
H – 4'	7.36 t, 7.6	128.98 d	
Glc – 1 – H	5.69 d, 7.6	99.40 d	
– 2 – H	4.50 dd, 9.2, 7.6	77.80 d	
– 3 – H	4.38 t, 9.2	79.07 d	
– 4 – H	4.35 t, 9.2	74.01 d	
– 5 – H	4.04 ddd, 9.2, 4.8, 2.4	78.75 d	
– 6 – H$_a$	4.42 dd, 12.0, 2.4	62.03 t	
– 6 – H$_b$	4.33 dd, 12.0, 4.8		
Rha – 1 – H	6.38 s,	102.36 d	Glc – 2 – C, Rha – 3, 5 – C
– 2 – H	4.79 br s	72.31 d	
– 3 – H	4.54 dd, 9.6, 2.8	72.68 d	
– 4 – H	4.26 t, 9.6	71.10 d	
– 5 – H	4.76 dq, 9.6, 6.0	69.81 d	
– 6 – Me	1.78 d, 6.0	18.78 q	

References

Akabori S, Akabori Y, Hasegawa M, 1980. Further structural studies of 1 – indanone derivatives obtained from *Onychium japonicum* [J]. *Chem Pharm Bull* , **28** (4): 1311 ~ 1313

Banerji A, Ramakrishnan G, Chadha M S, 1974. Onitin and onitisin, new phenolic pterosins from the fern *Onychium auratum* [J]. *Tetrahedron Letters* , **15**: 1369 ~ 1370

Hasegawa M, Akabori Y, Akabori S, 1974. New indanone compounds from *Onychium japonicum* [J]. *Phytochemistry* , **13** (2): 509 ~ 511

Hseu T H, Wang J L, Tang C P, 1980. The structure of onychiol B, [1aS, 3aS – (1β, 1aα, 3aβ, 5α, 5aα, 6α, 10aβ)] – 1 – [1 – (methoxymethyl) vinyl] – 3a, 5a, 8 – trimethyl – 2, 3, 3a, 4, 5, 5a, 9, 10, 10a, 10b – decahydro – 1H, 6H – cyclohept [e] indene – 5, 6 – diol: a diterpene alcohol from *Onychium japonicum* (Thunb.) Kunze [J]. *Acta Crystallogr* . **B36** (11): 2802 ~ 2804

Kokkalou E, Kapetanidis I, 1988. Flavonoids of the aerial parts of *Acinos suaveolens* [J]. *Pharm Acta Helv* , **63** (6): 170 ~ 173

Markham K R, Ternal B, Stanley R *et al* , 1978. Carbon – 13 NMR studies of flavonoids – III, naturally occurring flavonoid glycosides and their acylated derivatives [J]. *Tetrahedron* , **34** (9): 1389 ~ 1397

Nomura T, Fukai T, Katayanagi M, 1978. Kuwanon D, new isoprenoid flavanone from the root bark of the cultivated mulbery (*Morus alba* L.) [J]. *Heterocycle* , **9** (6): 745 ~ 752

Ramakrishnan G, Banerji, Chadha M S, 1974. Chalcones from *Onychium auratum* [J]. *Phytochemistry* , **13** (10): 2317 ~ 2318

Roitman J N, Wong R Y, Eckhard Wollenweber E, 1993. Methylene bisflavonoids from frond exudate of *Pentagramma triangularis* ssp. *triangularis* [J]. *Phytochemistry* , **34** (1): 297 ~ 301

Sengupta P, Sen M, Niyogi S K et al, 1976. Isolation and structure of wallichoside, a nevel pteroside from *Pteris wallichiana* [J]. *Phytochemistry* , **15** (6): 995 ~ 998

Wagner H, Chari V M, Sonnenbichler J, 1976. ^{13}C – NMR – Spectren naturlich vorkommender flavonoide [J]. *Tetrahedron Letters* , **21**: 1799 ~ 1802

Xu Y L, Kubo I, Ma Y B, 1993. A cytotoxic flavanone glycoside from *Onychium japonicum* : Structure of onychin [J]. *Phytochemistry* , **33** (2): 510 ~ 511

Xu Y L, Ma Y B, Xiong J, 1999. Flavonoids of *Onychium contiguum* [J]. *Acta Botanica Yunnanica* (云南植物研究), **21** (3): 386 ~ 392

Zhou Y H, 1988. Chemotaxonomy of Medicinal Plants [M]. Shanghai: Science and Technology Press, 219 ~ 222